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PRODUCTION OF DIALKYL CARBONATES

[Diarukiru Kaboneto no Seizo Hoho]

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SPECIFICATION

I. Title of the Invention

Production of Dialkyl Carbonates

II. Claims

1. A production method for dialkyl carbonates, characterized in that it reacts a cyclic carbonate and an alcohol in the presence of a solid strongly basic anion exchanger having a quaternary ammonium group as exchange group.

2. The production method of dialkyl carbonates according to Claim 1, wherein the anion is at least one anion selected from Cl^-, Br^-, HCO_3^-, CO_3^{2-}.

III. Detailed Description of the Invention

(Field of Industrial Application)

The present invention relates to a production method for dialkyl carbonates. In more detail, the present invention relates to a production method for dialkyl carbonates made by reacting a cyclic carbonate and an alcohol.

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[1]Numbers in the margin indicate pagination in the foreign text.

(Prior Art)

Various proposals concerning production methods for dialkyl carbonates by reacting a cyclic carbonate and an alcohol in the presence of a catalyst exist. For example, a method of using a tertiary aliphatic amine as catalyst (Japan Tokkyo S59-28542), a method of using an alkali metal or an alkali metallic compound as catalyst (USP 3,642,858), a method of using thallium compound (Japan Tokkyo 60—27658) as catalyst, a method of using tin alkoxides (Japan Tokkyo 56-40708) as catalyst, a method of using a composite catalyst comprising a Lewis acid and a nitrogen-containing organic base (Japan Tokkyo 60-22698), a method of using a quaternary phosphonium salt (Japan Kokai 56-10144) as catalyst, etc. are well known.

(Problems to Be Solved by the Invention)

As catalysts employed in the production method of dialkyl carbonates by reaction of a cyclic carbonate and an alcohol, homogeneous catalysts were mainly used previously. However, when a homogeneous catalyst was used, it was difficult to separate a reaction mixture and the catalyst. On the other hand, usually,

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distillation is necessary for obtaining dialkyl carbonates as product. Accordingly, when a homogeneous catalyst is used, a reaction mixture is heated and distilled while the catalyst remains as it is. As a result, dehydrating condensation of glycols being by-products and the like occur, thus the selectivity reduces.

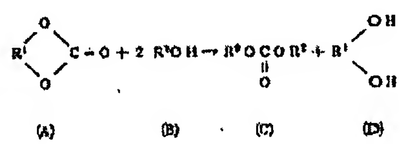
Although a method of reducing the amount of catalyst used is given to prevent it (Japan Tokkyo 61-45616), the reaction speed lowers. Moreover, side reactions during separation operations can also be substantially eliminated by using a solid catalyst as catalyst. As such possible catalysts, a silica-titania solid acid catalyst (Japan Tokkyo 61-5467) and a weakly basic exchange resin containing a tertiary aliphatic amino group (Japan Tokkyo 59-28542) has been known, but the catalytic activity is not enough and the reaction speed is low.

(Means for Solving the Problems)

The inventors earnestly studied catalysts used in the production of dialkyl carbonates by reacting a cyclic carbonate and an alcohol, consequently they discovered a novel catalyst which facilitated the separation from reaction solution and sustained a high activity for a long time and thus came to accomplish the present invention.

Namely, the present invention provides a production method of dialkyl carbonates characterized by reacting a cyclic carbonate and an alcohol in the presence of a solid strongly basic anion exchanger having a quaternary ammonium group as exchange group.

In the present invention, as shown in the following formula, a well-known reaction for obtaining a dialkyl carbonate (C) and a glycol (D) by reacting two molecules of alcohol (B) with a cyclic carbonate (A) may be applied as it is.



In the above formula, R^1 is a divalent group $-(CH_2)_m-$ (m is an integer 2 ~ 6) and may also be substituted by a C_1 ~ C_8 alkyl or aryl group, and R^2 is a C_1 ~ C_8 saturated or unsaturated hydrocarbyl group, etc.

The solid catalyst used in the present invention has higher activity than the prior solid catalysts. For example, the catalyst of present invention has higher activity than a basic resin containing a tertiary aliphatic amine described in Japan Tokkyo 59-28542. Although reasons for it have not been clarified

yet, the solid catalysts containing a quaternary ammonium group used in the present invention is inferred to have higher basicity than the tertiary amine.

The solid catalyst is also characterized in that activity deterioration in case of long-term use is less than in the case of the above basic resins containing a tertiary aliphatic amine. Reasons for it have also not been clarified yet. However, commonly-used cyclic carbonates are synthesized by adding carbon dioxide to corresponding epoxides, and contain a very small quantity of carbon dioxide as acid impurity. Accordingly, the rate of activity deterioration is considered to be low because the exchange rate of an acid anion to a quaternary ammonium group is smaller than the adsorption of an acid to a tertiary aliphatic amine.

The catalyst of present invention is a solid catalyst; therefore, the separation of catalyst from reaction solution is extremely easy. Namely, when the reaction is conducted by a batch-type reactor, the separation from the catalyst is made possible by filtration or decantation. When a tubular circulation reactor is used, only the reaction solution can be withdrawn by packing the solid catalyst of present invention into a reactor as a fixed bed.

The following are given for the effect of facilitating the separation of reaction solution and catalyst by using a solid catalyst. Namely, when a homogeneous catalyst is used, a product is obtained by distilling a reaction solution containing the catalyst, but glycols, being reaction by-products, cause dehydrating condensation due to this operation. If the reaction solution and the catalyst can be separated beforehand, a reduction of selectivity caused by such an undesirable reaction can be avoided.

As cyclic carbonates used in present invention, for example, alkylene carbonates such as ethylene carbonate, propylene carbo

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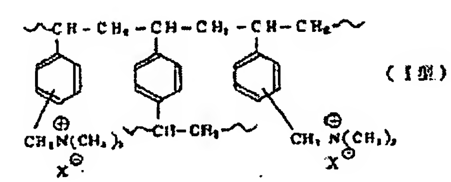
nate, etc., 1,3-dioxacyclohexan-2-one, 1,3-dioxacyclopentan-2-one, etc. are preferably used, ethylene carbonate and propylene carbonate are more preferably used from a viewpoint of ease of availability, etc.

As alcohols, for example, C_1 ~ C_{12} alcohols such as methanol, ethanol, propanol, 1-methylethanol, allyl alcohol, 1-buta-nol, 2-butanol, 2-methyl-2-propanol, 3-butene-1-ol, cyclohexanol, etc. are preferably used.

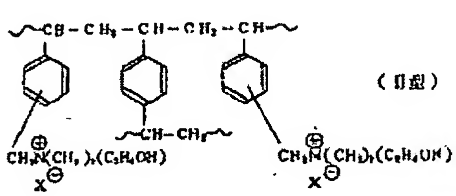
The solid strongly basic anion exchangers with quaternary ammonium groups as their exchange group used in the present invention may be any solid strongly basic anion exchangers, for

example, a strongly basic anion exchange resin with quaternary ammonium groups as exchange groups, a cellulose strongly basic anion exchanger with quaternary ammonium groups as exchange groups, an inorganic carrier support-type strongly basic anion exchanger with quaternary ammonium groups as exchange groups, etc. are given.

As solid strongly basic anion exchange resins with quaternary ammonium group as exchange groups, for example, styrene strongly basic anion exchange resins, etc. are preferably used. The styrene strongly basic anion exchange resin is a strongly basic anion exchange resin with a styrene-divinylbenzene copolymer as parent body and quaternary ammonium groups (type I or type II) as exchange groups, for example, they are typically shown by the following formulas.



(type I)



(type II)

In the above formulas, X^- represents an anion, at least one anion selected from F^-, Cl^-, Br^-, I^-, HCO_3^-, CO_3^{2-}, $CH_3CO_2^-$, CO_3^{2-}, HCO_2^-, IO_3^-, BrO_3^-, ClO_3^- is commonly used as X^- and at least one anion selected from Cl^-, Br^-, HCO_3^-, CO_3^- is preferably used as X^-. As structures of resin parent body, both gel type and macro-reticular type (MR type) can be used, but MR type is more preferable from a viewpoint of high organic solvent resistance.

As cellulose strongly basic anion exchangers with quaternary ammonium groups as exchange groups, for example, celluloses with an exchange group made of $-OCH_2CH_2N^+R_2X^-$ obtained by alkylaminoethylation of a part or all of the OH groups of cellulose are given. However, R represents an alkyl group, methyl, ethyl, propyl, butyl, etc. are commonly used, and methyl, ethyl are preferably used. X^- is as described above.

An inorganic carrier support-type strongly basic anion exchanger with quaternary ammonium groups as exchange groups usable in the present invention means quaternary ammonium groups $-O(CH_2)_nN^+R_3X^-$ introduced by modifying a part or all of surface hydroxyl groups -OH of an inorganic carrier. However, R, X^- are as described above. n is commonly an integer of 1 ~ 6, preferably n = 2. As inorganic carriers, silica, alumina, silica-alumina, titania, zeolite, etc. can be used, silica, alumina, silica-alumina are preferably used, and silica is more

prefer-ably used. Any methods can be used as methods for modifying the surface hydroxyl groups of the inorganic carrier. For example, they are aminoalkoxylated by conducting dehydration of an inorganic carrier and an aminoalcohol $HO(CH_2)_nNR_2$ in the presence of a basic catalyst, then reacted with an alkyl halide RX′ (X′ represents a halogen atom, and Cl, Br, I, etc. are commonly used) to make them into $-O(CH_2)_nN^+R_3X^-$. They are further made into quaternary ammonium groups $-O(CH_2)_nN^+R_3X^-$ having a desirable anion X^-. In case of n = 2, the groups are N,N-dialkylaminoethoxylated

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by treatment with N,N-dialkylaziridine to make them into an $-OCH_2CH_2NR_2$ groups and then made them into$-O(CH_2)_nN^+R_3X^-$ having by the above method.

Commercial solid strongly basic anion exchanger with quaternary ammonium groups as exchange groups can also be used. In that case, the exchanger is ion-exchanged with a desirable anion species beforehand as a pretreatment and then can be used as catalyst.

The solid strongly basic anion exchanger with quaternary ammonium groups as exchange groups can be used in a state of containing water. However, if water is mixed into the reaction system, ethylene carbonate as starting material and dimethyl

carbonate as product are hydrolyzed, therefore it is preferable that the exchanger is dried beforehand and then used as catalyst. As drying methods, for example, a method for dehydrating it by heating under a withstand temperature and a reduced pressure, a method for removing water by boiling at a temperature under the withstand temperature with an azeotropic solvent forming minimum azeotropic mixture with water, such as benzene, toluene, ethylbenzene, etc. are used.

The above strongly basic anion exchanger is commonly used as powdery or spherical or columnar particles with mean particle diameter of 0.2 ~ 10 mm.

As reaction modes, commonly-used methods such as fluid-bed type, fixed-bed type or agitation-type, etc. can be employed. Either flow type or batch type method may be used, and the separation of reaction solution and catalyst can be easily carried out.

When the present invention is carried out, the reaction temperature is commonly 30 ~ 300°C, preferably 50 ~ 260°C. However, when the employed catalyst has an inherent withstand temperature, the reaction is preferably conducted in a temperature range thereunder.

The reaction time can also vary with the kind and compositional ratio of cyclic carbonate and alcohol and the reaction

temperature, for example, it is expressed as a liquid hourly space velocity (LHSV) to the total feed liquid in case of a flow reaction, 0.05 ~ 40 hr^{-1} is commonly used, preferably 0.2 ~ 20 hr^{-1}, and more preferably 0.2 ~ 10 hr^{-1}. In case of a batch reaction, it is commonly 0.05 ~ 60 hr^{-1}, preferably 0.1 ~ 40 hr^{-1}, and more preferably 0.2 ~ 20 hr^{-1}.

The ratio of cyclic carbonate being starting material to alcohol can be used within a wide range. However, if the mole ratio of alcohol to cyclic carbonate is too large, the quantity of recovered alcohol is too large and not realistic. If the mole ratio is too small, the conversion of cyclic carbonate is too low, therefore the recovery increases and is still not realistic. Accordingly, the mole ratio of cyclic carbonate being starting material to alcohol is commonly 0.05 ~ 100, preferably 0.1 ~ 40, and more preferably 0.2 ~ 20.

(Effects of the Invention)

By the invented method, dialkyl carbonates can be obtained in a high selectivity with a cyclic carbonate and an alcohol, and high activity sustains for a long time. The separation of reaction solution and catalyst is also easy.

(Actual Examples)

The present invention is specifically described by showing actual examples below.

Actual Example 1

(Pretreatment of catalyst)

The pretreatment of Dowex MSA-1 [a styrene strongly basic anion exchange resin (type I) with anion species Cl^-, made by Dow Chemical Co.] is made by a method described below with anion species as Cl^-.

1) 500 mL of Dowex MSA-1 was stirred for 1 hr in 500 mL of a 4% aqueous NaOH solution, then filtered and washed with 5,000 mL of water.

2) It was further stirred for 1 hr in 500 mL of a 10% aqueous HCl solution, then filtered and washed with 5,000 mL of water.

3) 1) was repeated, and then 2) was repeated twice.

4) Residual water was removed to give a catalyst A by heating the resin treated by the above 1) ~ 3) together with 500 mL of ethylbenzene (120°C) and removing water at azeotropic composition. Excessive ethylbenzene was removed by decantation, and

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then the catalyst was stored in dry methanol.

(Reaction)

The catalyst A obtained above was packed in a tubular reactor (12.7 mm in outside diameter and 57 mL in inner volume), and methanol was delivered into the reactor at room temperature. Methanol was delivered until ethylbenzene in the delivered methanol was almost not detected by gas chromatographic analysis (less than 0.01 wt% by ethylbenzene concentration in methanol). A mixed solution of methanol and ethylbenzene carbonate (synthesized from ethylene oxide and carbon dioxide and abbreviated as EC) (mole ratio of MeOH/EC = 5) was started to deliver at a flow rate of 110 mL/hr (LHSV = 3 hr^{-1}), and the reactor was heated to 100°C in a state of keeping the pressure of reaction system to 7 kg/cm^2 (gage pressure). Analysis of delivered reaction solution was made at a time that the reaction system became stationary. As a result, the conversion of ethylene carbonate was 48%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively. Cl^- and other anion and cation species did not exist in the reaction solution. The flow reaction was continued as it was, and analysis of reaction solution delivered after 120 hr since a time that reaction became stationary. As a result, the conversion of ethylene carbonate was 49%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Comparison Example 1

Water was removed by heating 1]ϑ⊥-Ξ=Δ A-21 [trade-name, tertiary aliphatic amine type (free base type), made by Rohm & Haas Co.) to 60°C under reduced pressure. The reaction was conducted by the same method as Actual Example 1 except that this catalyst was used. The conversion of ethylene carbonate was 32%, the selectivity of dimethyl carbonate was 98%, and the selectivity of ethylene glycol was 98%. The flow reaction was continued as it was, and analysis of reaction solution delivered after 116 hr since a time that reaction became stationary was made. As a result, the conversion of ethylene carbonate was 18%, the selectivity of dimethyl carbonate was 92%, and the selectivity of ethylene glycol were 85%.

Actual Example 2

The reaction was conducted by the same method as Actual Example 1 except that it was conducted at reaction temperature of 120°C and LHSV = 2 hr^{-1}. The conversion of ethylene carbonate was 58%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Actual Example 3

Water was removed by heating Dowex MSA-1 under reduced pressure (20 torr) to give a catalyst B. The reaction was con-

ducted by the same method as Actual Example 1 except that this catalyst B was used. The conversion of ethylene carbonate was 44%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Actual Example 4

(Pretreatment of catalyst)

1) 500 mL of Dowex MSA-1 was stirred for 1 hr in 500 mL of a 4% aqueous NaOH solution, then filtered and washed with 5,000 mL of water.

2) 1) was further repeated twice.

3) Residual water was removed to give a catalyst C having a HCO_3^- group as anion by heating the above resin together with 500 mL of toluene and distilling toluene and water at azeotropic composition.

(Reaction)

The reaction was conducted by the same method as Actual Example 1 except that the catalyst C was used. The conversion of ethylene carbonate was 50%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Actual Example 5

(Pretreatment of catalyst)

A catalyst D having a CO^{2-}_3 group as anion was obtained by the same method as Actual Example 4 except that sodium carbonate was used in place of sodium hydrogen carbonate.

(Reaction)

The reaction was conducted by the same method as Actual Example 1 except that this catalyst D was used. The conversion

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of ethylene carbonate was 52%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Actual Example 6

The reaction was conducted by the same method as Actual Example 1 except that triethylaminoethyl cellulose (made by Selva Co.) with anion species as Cl^- was used as catalyst. The conversion of ethylene carbonate was 41%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Actual Example 7

The reaction was conducted by the same method as Actual Example 1 except that a hydrophilic silica gel (quaternary aminoethyl type, TSK-GELQAE-2SW, made by Toyo Soda Co., anion species Cl^-) was used as catalyst. The conversion of ethylene carbonate

was 43%, and the selectivity of dimethyl carbonate and ethylene glycol were 99%, 99%, respectively.

Actual Example 8

0.50 mole of ethylene carbonate, 2.0 mole of methanol and 1.0 g of a catalyst A (crushed to 80 ~ 100 mesh) were added into an autoclave of 300 mL in volume, the inside of system was replaced with N_2, then stirring and heating were started to make the system to a reaction temperature of 100°C. After 1 hr, the autoclave was cooled, reaction solution was filtered and separated from the catalyst. A distillate and a distillation residue were obtained by distilling this filtrate under normal pressure and reduced pressure. 0.269 mole of ethylene carbonate, 0.215 mole of dimethyl carbonate and 0.215 mole of ethylene glycol were contained in the distillate. Only 0.016 mole of ethylene carbonate existed in the distillation residue. This result indicated that the conversion of ethylene carbonate was 45%, the selectivity of dimethyl carbonate was 99%, and the selectivity of ethylene glycol was 99%.

Comparative Example 2

0.50 mole of ethylene carbonate, 2.0 mole of methanol and 0.005 mole of sodium methoxide as catalyst were added into an autoclave of 300 mL in volume, the inside of system was replaced with N_2, then stirring and heating were started to make the

system to a reaction temperature of 100°C. After 30 min, when the autoclave was cooled and the reaction solution was analyzed, sodium methoxide was homogeneously dissolved in the reaction solution. A distillate and a distillation residue were obtained by distilling this reaction solution under normal pressure and reduced pressure. 0.260 mole of ethylene carbonate, 0.216 mole of dimethyl carbonate and 0.168 mole of ethylene glycol were contained in the distillate. 0.015 mole of ethylene carbonate and a high-boiling by-product existed in the distillation residue. This result indicated that the conversion of ethylene carbonate was 45%, the selectivity of dimethyl carbonate was 97%, and the selectivity of ethylene glycol was 75%.

Actual Example 9

The reaction was conducted by the same method as Actual Example 1 except that propylene carbonate was used in place of ethylene carbonate. The conversion of propylene carbonate was 51%, the selectivity of dimethyl carbonate and propylene glycol was 99%, 99%, respectively.

Actual Example 10

The reaction was conducted by the same method as Actual Example 4 except that ethanol was used in place of methanol. The conversion of ethylene carbonate was 53%, the selectivity of

dimethyl carbonate and ethylene glycol was 99%, 99%, respectively.

Actual Example 11

The reaction was conducted by the same method as Actual Example 5 except that allyl alcohol was used in place of methanol. The conversion of propylene carbonate was 42%, the selectivity of dimethyl carbonate and ethylene glycol was 99%, 99%, respectively.

Actual Example 12

A catalyst E containing Br^- as anion was obtained by the catalyst pretreatment method of Actual Example 1 except that a 10% aqueous HBr solution was used in place of a 10% aqueous HCl solution. The reaction was conducted with this catalyst under the same conditions as Actual Example 1. The conversion of propylene carbonate was 50%, the selectivity of dimethyl carbonate and ethylene glycol was 99%, 99%, respectively.